

Changes in Phosphorus Fractions in Soils under Intensive Plant Growth

F. Guo, R. S. Yost,* N. V. Hue, C. I. Evensen, and J. A. Silva

ABSTRACT

The total quantity of P and plant-available P often differ greatly in soils of the tropics, which typically range in weathering intensity. Assessing available P is fundamental to managing P in many of these soils. Phosphorus availability in some soils has been inferred from the Hedley sequential extraction assuming that each P fraction reflects similar plant availability in different soils. However, experimental measurements of plant P availability were either of short duration or involved multiple P applications, which complicates assessment of the plant availability of P fractions. The objectives of this study were to examine the changes in P fractions under exhaustive cropping on diverse soils and to discern the differences in plant availability among P fractions. Eight soils ranging in weathering from Vertisols and Mollisols to Ultisols and Oxisols were amended with $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ to raise soil solution P to 0.2 mg L^{-1} and planted for 14 crops to remove available P. The results indicated that the Fe-impregnated strip-P and inorganic $\text{NaHCO}_3\text{-P}$ ($\text{NaHCO}_3\text{-P}_i$) decreased the most in response to plant P withdrawal in all soils. The inorganic NaOH-P (NaOH-P_i) also declined with plant P uptake in all soils. The HCl-P and residual P seemed to act as a buffer for the strip-P and the $\text{NaHCO}_3\text{-P}$ in the slightly weathered soils, whereas NaOH-P_i seemed to act as a buffering pool for strip-P and $\text{NaHCO}_3\text{-P}_i$ in the highly weathered soils. Residual P in the slightly weathered soils was plant-available on a relatively short time scale. In contrast, residual P in the highly weathered soils accumulated in the presence of intensive plant P removal, indicating that it was unavailable to plants. Organic P ($\text{NaHCO}_3\text{-P}_o$ and NaOH-P_o) fractions were not significant contributors to available P in these soils that received high levels of inorganic P. Phosphorus fractions separated by the same sequential method were not of equal availability to plants in all soils.

THE COMPLEX CHEMISTRY and spatial variability of P in soils make direct identification of P compounds and assessment of plant availability difficult (Hsu, 1965; Sawhney, 1973; Webber, 1978; Pierzynski et al., 1990a, 1990b, 1990c). The Hedley fractionation method has been widely used to characterize soil P availability. The procedure, in its original (Hedley et al., 1982) or modified forms (Tiessen et al., 1983, 1984; Sharpley et al., 1987; Tiessen and Moir, 1993; Beck and Sanchez, 1994), removes the readily available P from the soil first with mild extractants, then the more stable P forms with stronger extractants. The basic assumption of the procedure is that extractants of varying strength estimate P fractions of differing availability (Hedley et al., 1982), and that a specific fraction is of similar availability in different soils. This assumption needs to be verified in order to improve P management models such as the PDSS2 (Phosphorus Decision Support System; Yost et al., 1992).

Soil P was fractionated by the original Hedley procedure into eight fractions, which included a microbial P fraction using chloroform and dilute NaHCO_3 (pH 8.5). Although Hedley et al. (1982) indicated that microbial P may be estimated in their Mollisol (Udic Haploboroll) with an empirical recovery factor (Hedley et al., 1982), a later study suggested that Hedley's original scheme underestimated microbial P in tropical soils when soils are allowed to dry (Potter et al., 1991). Microbial P is highly variable and one of the smaller fractions in most soils. Thus, many later procedures omitted the chloroform-bicarbonate extraction for estimating microbial P, and only seven fractions were estimated (Tiessen et al., 1983, 1984; Tiessen and Moir, 1993; Beck and Sanchez, 1994; Schmidt et al., 1996).

The Hedley procedure has been used to study P fractions in both slightly weathered (Hedley et al., 1982; Tiessen et al., 1983; O'Halloran et al., 1987; Richards et al., 1995) and highly weathered soils (Ball-Coelho et al., 1993; Agbenin and Tiessen, 1994; Beck and Sanchez, 1994; Schmidt et al., 1996). Phosphorus fraction changes due to organic amendments have also been reported (Hedley et al., 1982; Iyamuremye et al., 1996; Leinweber, 1996). Most authors seemed to agree that the P extracted by the anion exchange resin or Fe-impregnated strips and the $\text{NaHCO}_3\text{-P}_i$ are plant available. However, the availability of the other fractions is less certain. Various interpretations, reflecting tremendous uncertainty in the availability of these fractions, suggested by different authors have been summarized by Cross and Schlesinger (1995). The focus of previous work was on measuring P fractions under different P treatments or cultural practices; less attention was given to the dynamic changes of P fractions during an extended period of time. A few recent studies measured P fraction changes under extended plant P removal (Ball-Coelho et al., 1993; Beck and Sanchez, 1994; Richards et al., 1995; Schmidt et al., 1996), but changes of P fractions were masked by repeated P additions, which resulted in a complex storing and removal of P fractions and in altered patterns of P fraction change that complicate assigning P availability on the basis of plant P removal. Hypotheses tested were (i) that the soil P continuum could be separated into discrete fractions of differing availability and (ii) that the availability of the fractions would be consistent in soils of differing degrees of weathering. Therefore, the objectives of this study were to examine the changes in P fractions under exhaustive cropping on diverse soils and to compare the plant availability of the Hedley P fractions in eight soils under intensive plant growth.

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Table 1. Taxonomy and selected physical properties of the soils used in this study.

Series	Subgroup	Sand ($>45\ \mu\text{m}$)	Silt ($2-45\ \mu\text{m}$)	Clay ($<2\ \mu\text{m}$)	Water content	
					$-0.03\ \text{MPa}$	$-1.5\ \text{MPa}$
				g kg^{-1}		
Honouliuli	Typic Chromustert	56.5	363.6	580.0	350.4	226.3
Lualualei	Typic Chromustert	49.9	161.7	788.4	440.7	286.0
Nohili	Cumulic Haplaquoll	26.8	166.6	806.6	550.2	371.1
Paaloa	Rhodic Kandudult	53.8	205.4	740.8	405.4	284.7
Wahiawa	Rhodic Eutruxox	20.4	84.6	895.0	439.4	317.9
Kapaa	Anionic Acrudox	91.5	383.4	525.1	380.8	242.1
Leilehua	Ustic Kanhaplohumult	17.0	120.2	862.9	455.3	313.4
Mahana	Humic Rhodic Haplustox	146.1	367.6	486.3	445.1	261.6

MATERIALS AND METHODS

Soil Characterization

Eight soils, representing a wide range in weathering (Tables 1–3) and P sorption (Table 4), were sampled from 0 to 15 cm in depth except for the Kapaa soil, for which both surface and subsurface horizons were sampled and mixed. The soil samples were composited from three subsamples. The soils were ground to pass a 0.84-mm sieve, and the following measurements were taken: pH in 1:1 soil/water suspension, organic C (Nelson and Sommers, 1982), particle size (Gee and Bauder, 1986), and calcium carbonates (Nelson, 1982). Water content at -0.03 and $-1.5\ \text{MPa}$ was measured using pressure plates by presoaking the soil materials in water overnight. Soil available water capacity was calculated as the difference between the matrix potentials of -0.03 and $-1.5\ \text{MPa}$. Clay mineral contents were estimated by the Rietveld refinement using the SIROQUANT computer program (Sietronics Pty. Ltd., 1993). X-ray amorphous content of the clay was determined by the Rietveld refinement method in the same manner as in measuring minerals after spiking the clay with alumina powder (Jones et al., 2000).

Soil Incubation

Soils were air-dried and ground to pass a 4-mm sieve using a mechanical grinder. Acidic soils were limed to pH 6.5 by adding laboratory-grade, powdered CaCO_3 . After liming, the soils were moistened to their available water capacity (soil water between matrix potential of -0.03 and $-1.5\ \text{MPa}$) and incubated for 4 wk in plastic bags. Five-kilogram (dry basis) portions of each soil were weighed onto clean brown paper. The prescribed amount of P as $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Table 4) was thoroughly mixed with the soil. The treated soils were then placed into plastic pots (18 cm in diameter, 30 cm deep), and watered weekly with deionized water to available water capacity and allowed to dry during the week in the greenhouse

for 4 wk. At 60 d after P application, $50\ \text{mg N kg}^{-1}$ as urea, $60\ \text{mg K kg}^{-1}$ as KCl, $25\ \text{mg kg}^{-1}\ \text{Mg}$ as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and $5\ \text{mg kg}^{-1}\ \text{Zn}$ as $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, were added into each pot and mixed. The experimental design was a randomized complete block with three replicates of each soil.

Soil Fractionation

Soil samples were sequentially extracted for P using a modified Hedley procedure. Triplicate 0.5000-g samples were weighed into 40-mL screw-capped centrifuge tubes, and 30.0 mL of extractant were added and the tubes were shaken for 45 min of each hour for 16 h. The extractants, in sequential order, were: (i) 30 mL of deionized water and one 2 by 10 cm Fe-impregnated strip as prepared according to Guo et al. (1996), (ii) $0.5\ \text{M NaHCO}_3$ at pH 8.5, (iii) $0.1\ \text{M NaOH}$, (iv) $1\ \text{M HCl}$, and (v) 5.0 mL of concentrated H_2SO_4 ($\approx 18\ \text{M}$) and 2 to 3 mL of H_2O_2 ($300\ \text{g kg}^{-1}$) in 0.5-mL increments. Inorganic P (P_i) in the extracts was determined by the method of Murphy and Riley (1962) after pH adjustment using nitrophenol as an indicator. Total P (P_T) was also measured in both the NaHCO_3 and the NaOH extracts for calculating organic P (P_o). P_T was determined with the Murphy and Riley (1962) method after autoclave digestion to convert P_o to P_i with acid ammonium peroxysulfate as described in the Standard Methods (American Public Health Association, American Water Works Association, and Water Environment Federation, 1995). Organic P was calculated as the difference between P_T and P_i in the extracts. Total soil P was determined by the Na_2CO_3 fusion method (Olsen and Sommers, 1982).

Cropping

Corn (*Zea mays* L.) was grown for Crops 1 to 10, 13, and 14. Crops 11 and 12 were soybean [*Glycine max* (L.) Merr.]. When corn was grown, each pot received 12 pregerminated corn seeds (Hybrid X304CF15, Pioneer Hi-Bred Int., John-

Table 2. Selected chemical properties of the soils used in this study.

Soil	pH (H_2O , 1:1)	Organic C	Carbonates (as CaCO_3)	Total exch. cations†	$\text{Fe}_{ox}\ddagger$	$\text{Al}_{ox}\ddagger$	Total P§	0.5 M NaHCO_3 ¶ extractable P
		g kg^{-1}		cmol kg^{-1}		g kg^{-1}		mg kg^{-1}
Honouliuli	7.26	16.6	3.2	30.6	3.40	1.43	1.840	26.3
Lualualei	7.65	4.1	16.2	106.8	3.82	2.94	2.098	31.9
Nohili	7.44	17.1	65.8	109.5	11.80	4.32	0.815	3.2
Paaloa	5.05	40.0	0#	5.5	7.48	2.98	0.596	1.1
Wahiawa	5.05	35.8	0#	4.1	3.27	3.65	0.528	1.6
Kapaa	4.92	45.6	0#	3.8	4.54	5.61	1.722	2.5
Leilehua	4.66	44.0	0#	1.0	6.56	6.50	0.699	1.2
Mahana	4.31	36.7	0#	1.4	5.70	12.81	1.327	15.8

† $1\ \text{M NH}_4\text{OAc}$ method (Thomas, 1982).

‡ ox denotes acid ammonium oxalate extraction (Hodges and Zelazny, 1980).

§ Na_2CO_3 fusion (Olsen and Sommers, 1982).

¶ Olsen and Sommers (1982).

Not measured, CaCO_3 assumed to be zero because this is a highly acid soil.

Table 3. Mineralogical composition of soil clay (<2 μm) fraction of the soils used in this study.

Minerals	Soil series							
	Honouliuli	Lualualei	Nohili	Paaloa	Wahiawa	Kapaa	Leilehua	Mahana
	g kg ⁻¹							
Anatase	—†	—	—	49	35	49	—	—
Calcite	—	74	28	—	—	—	—	—
Dolomite	—	—	46	—	—	—	—	—
Gibbsite	—	—	—	76	86	34	50	17
Goethite	—	51	—	88	47	363	103	76
Halloysite	621	—	—	—	—	145	—	—
Hematite	41	6	29	94	59	9	78	128
Illite	—	—	—	67	160	—	136	—
Kaolinite	—	245	249	232	292	—	284	344
Maghemite	—	—	—	19	—	7	—	—
Quartz	—	15	—	20	8	—	12	17
Smectite	—	148	161	—	—	—	—	—
Amorphous†	338	460	486	356	314	393	338	419
Amorphous§	24	13.4	25.9	63.9	41.3	72.2	79.6	91.7

† Not detected.

‡ Rietveld refinement with amorphous spike in clay (Jones et al., 2000).

§ Ammonium oxalate extraction in whole soil according to the method of Hodges and Zelazny (1980).

ston, IA), which were placed ≈ 1 to 2 cm below the soil surface. At 3 d after emergence (DAE), each pot was thinned to 10 seedlings. Two additional doses of N at 50 mg kg⁻¹ were applied at 10 and 20 DAE. Plants were grown for 4 wk. For the two soybean crops, five healthy, noninoculated, and presoaked seeds were placed 1 to 2 cm below the soil surface in each pot, and thinned to three seedlings in each pot 3 DAE. Nitrogen was applied at 56 mg kg⁻¹ and equally split between 0 and 15 DAE. Boron (as sodium borate) and molybdenum (as ammonium molybdate) were applied both at 0.9 mg kg⁻¹ in the first soybean crop. Other supplemental nutrients were added in amounts similar to those of corn. Soybean plants were grown for 45 d. The pots were watered daily with deionized H₂O, and moisture was maintained near soil available water capacity throughout the growth period.

A 2-g soil sample was taken from each pot after Harvests 2, 4, 6, 8, 10, 12, and 14. Roots were removed, and samples were dried and ground to pass a 0.25-mm sieve for sequential extraction.

F protected Fisher's LSDs at $\alpha = 0.05$ were calculated at each harvest with SAS for Windows, version 6.11, using the PROC MEANS statement (SAS Institute, 1996).

RESULTS AND DISCUSSION

The eight soils were divided into three groups according to their P sorption capacity (Table 4): (i) low P sorption soils that are slightly weathered alkaline soils (Table 2) with layer silicates as their dominant mineral-

Table 4. Phosphorus application rates for the greenhouse experiment.

Series	P added†
	mg P kg ⁻¹
Low P sorption soils	100
Honouliuli (Typic Chromustert)	
Lualualei (Typic Chromustert)	
Nohili (Cumulic Haplaquoll)	
Medium P sorption soils	500
Paaloa (Rhodic Kandudult)	
Wahiawa (Rhodic Eustrustox)	
High P sorption soils	1400
Kapaa (Anionic Acrudox)	
Leilehua (Ustic Kanhaplohumult)	
Mahana (Humic Rhodic Haplustox)	

† Amount required to raise solution P to 0.2 mg L⁻¹ according to the method of Fox and Kamprath (1970).

ogy (Table 3), (ii) medium P sorption soils that are acidic soils (Table 2) with a mixture of layer silicates and Fe and Al oxides, and (iii) high P sorption soils having very low pH and Fe and Al oxides as their dominant mineralogy (Tables 2 and 3). The sequential extraction method separates soil P into four inorganic, two organic, and a residual fraction that is perhaps a mixture of both inorganic and organic P.

Strip-Phosphorus and Inorganic NaHCO₃-Phosphorus

Neither the strips nor the 0.5 M NaHCO₃ solution sharply alters the soil, and their extraction power better mimics the extraction power of plant roots than other reagents used during fractionation. Estimated P from these two extractants was highly correlated with plant P uptake in previous studies (Bowman et al., 1978; van der Zee et al., 1987; Menon et al., 1989; Sharpley, 1991). The strip-P and the NaHCO₃-P_i are thus usually assumed to be plant available (Mattingly, 1975; Hedley et al., 1982; Tiessen et al., 1984; Cross and Schlesinger, 1995). The strip-P and the NaHCO₃-P_i in our soils were purposely elevated by adding a large dose of P to allow for extended cropping and also represent soils with high P buildup. Both strip-P and NaHCO₃-P_i declined with cropping in all soils, but the slopes of decline were different between strip-P and NaHCO₃-P_i for the same soil, and among soils with either extractant (Fig. 1). The decline in strip-P and NaHCO₃-P_i in the three slightly weathered soils (Fig. 1a and 1d) appeared to follow the same pattern, although the magnitude of decline was significantly different in the Nohili as compared with the other two soils, suggesting that strips and NaHCO₃ measured a similar P fraction in these soils (Fig. 1). The decline of strip-P and NaHCO₃-P_i in the highly weathered soils (Fig. 1b, 1c, 1e, and 1f) was different from that in the slightly weathered soils. Under intensive plant growth, strip-P in the highly weathered soils demonstrated an initial fast decline followed by a slower gradual decline (Fig. 1). The fast initial decline was not observed in the slightly weathered soils. The Paaloa

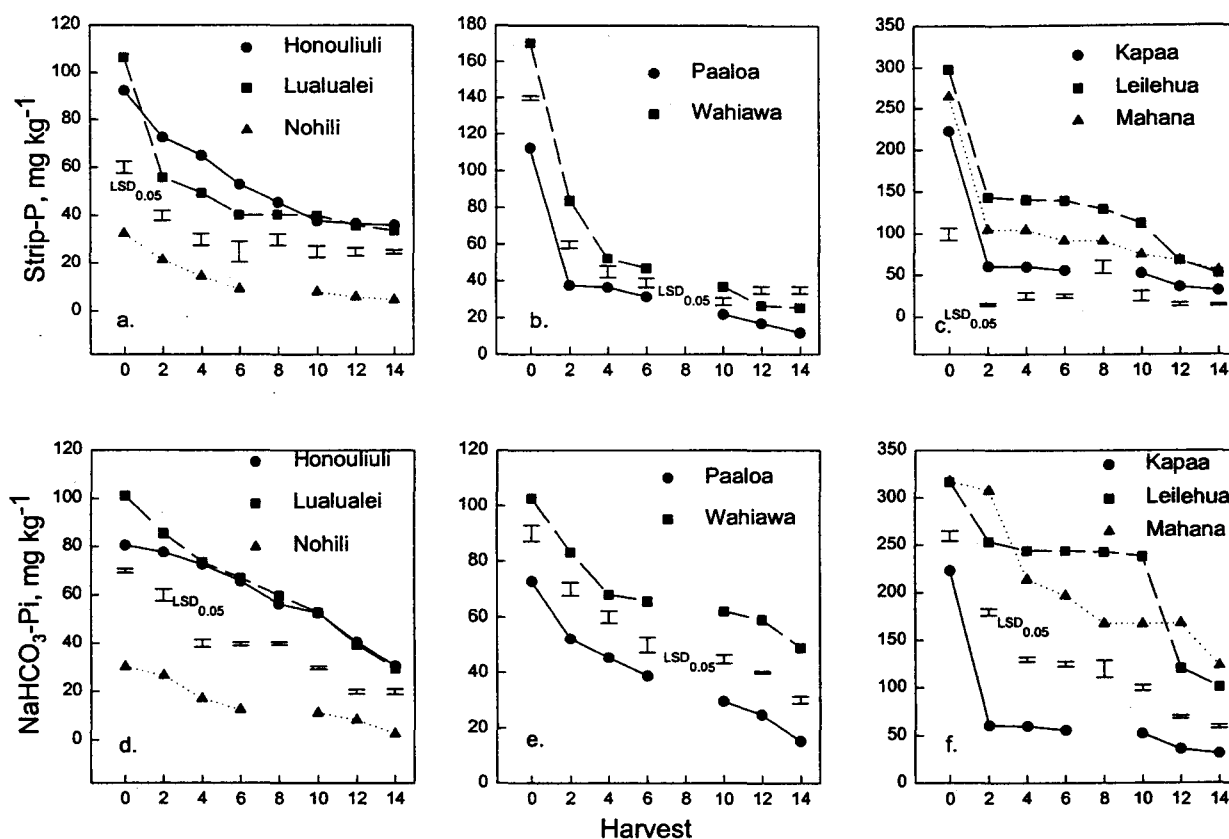


Fig. 1. Changes in inorganic strip- and $\text{NaHCO}_3\text{-P}_i$ in eight soils under exhaustive cropping. Phosphorus was added in each soil to raise soil solution P to 0.2 mg L^{-1} . Honouliuli, Lualualei, and Nohili were considered low P sorption soils and Paaloa and Wahiawa were medium P sorption soils, while the Kapaa, Leilehua, and Mahana soils were characterized by high P sorption.

and the Wahiawa soils had identical P sorption capacity (both requiring 500 mg kg^{-1} to attain 0.2 mg P L^{-1} solution P), but the Wahiawa soil contained significantly more strip-P and $\text{NaHCO}_3\text{-P}_i$ than the Paaloa soil (Fig. 1b and 1e). Mineralogical analysis indicated that the Paaloa had higher goethite and hematite content and fewer secondary layer silicates than the Wahiawa soil (Table 3). The parallel decline curves of the Paaloa and the Wahiawa soils seemed to suggest that both the strip-P and the $\text{NaHCO}_3\text{-P}_i$ in these two soils responded similarly to plant-available P removal. Among the three high P sorption soils (Fig. 1c and 1f), the decrease in both strip-P and $\text{NaHCO}_3\text{-P}_i$ was similar to that of the Paaloa and the Wahiawa (Fig. 1). Both the strip-P and $\text{NaHCO}_3\text{-P}_i$ were significantly different among the three soils after all harvests (Fig. 1c and 1f), with the Leilehua soil having the highest combined strip-P and $\text{NaHCO}_3\text{-P}_i$, and the Kapaa soil having the least. The strips and the NaHCO_3 extracted similar fractions in the three high P sorption soils (Fig. 1c and 1f). In all soils, both strip-P and $\text{NaHCO}_3\text{-P}_i$ appeared to strongly reflect plant P removal.

Inorganic Hydroxide-Extractable Phosphorus

The P_i extracted by 0.1 M NaOH is considered as P associated with Fe and Al (Hedley et al., 1982; Tiessen et al., 1984; Wager et al., 1986) through chemisorption

to surfaces of Fe and Al components (Ryden et al., 1977; McLaughlin et al., 1977). Williams et al. (1971) indicated that some Ca-P may also be extracted by NaOH. Although long-term measurements of its decline are rarely made, NaOH- P_i is often assumed to be moderately available (Hedley et al., 1982; Schmidt et al., 1996; Ivarsson, 1990). Changes of NaOH- P_i during the growth of the 14 crops are summarized in Fig. 2. Significant differences were found among soils of similar P sorption capacities (Fig. 2). In the slightly weathered soils (Fig. 2a), NaOH- P_i seemed to be associated with soil Fe oxides. The Nohili soil had the lowest content of Fe oxides and the least NaOH- P_i (Fig. 2a, Table 3). In the highly weathered soils (Fig. 2b and 2c), the amount of NaOH- P_i within each group seemed to be the opposite in ranking the soils with respect to the strip-P or the $\text{NaHCO}_3\text{-P}_i$. The Wahiawa soil contained more strip-P and $\text{NaHCO}_3\text{-P}_i$, but lower NaOH- P_i than the Paaloa soil. Among the three high P sorption soils (Fig. 2c), the Leilehua had the highest strip-P and $\text{NaHCO}_3\text{-P}_i$, but its NaOH- P_i was the lowest. The NaOH- P_i in the highly weathered soils was directly related to the soil amorphous content and to the sum of Fe oxides (Table 3). Inorganic NaOH-P was not a static fraction in any of the soils. Instead, it declined under cropping (Fig. 2). In the highly weathered soils (Fig. 2b and 2c), readily available soil P (strip-P and $\text{NaHCO}_3\text{-P}_i$) and NaOH- P_i appeared to be in equilibrium. When readily available

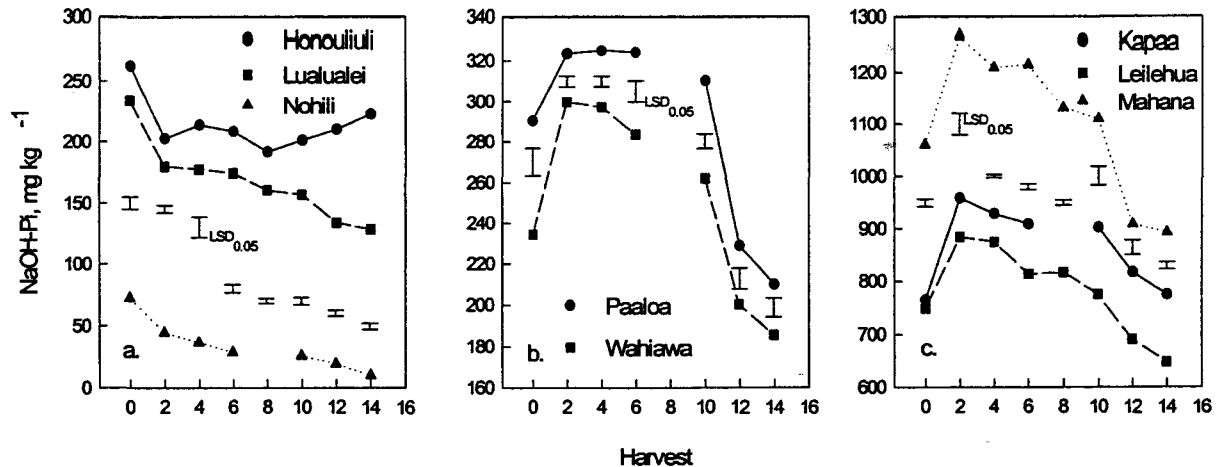


Fig. 2. Changes in NaOH- P_i in eight soils under exhaustive cropping. Phosphorus was added in each soil to raise soil solution P to 0.2 mg L^{-1} . Honouliuli, Lualualei, and Nohili were considered low P sorption soils and Paaloa and Wahiawa were medium P sorption soils, while the Kapaa, Leilehua, and Mahana soils were characterized by high P sorption.

P in soils was high, NaOH- P_i seemed to accumulate in soils with high Fe and Al oxides, as indicated by the increases in NaOH- P_i for the first two harvests (Fig. 2, Table 3). When strip-P and $\text{NaHCO}_3\text{-}P_i$ began to level off (Fig. 1 and 2), NaOH- P_i started to decline at a faster rate than in previous harvests (Fig. 2). Although NaOH- P_i may not be as available as strip-P or $\text{NaHCO}_3\text{-}P_i$, there is no clear-cut separation between $\text{NaHCO}_3\text{-}P_i$ and NaOH- P_i .

Organic Phosphorus

The $\text{NaHCO}_3\text{-}P_o$ and NaOH- P_o are usually estimated by the Hedley procedure. Although Hedley's procedure was found useful in characterizing the availability of soil P_o (Tiessen and Moir, 1993), the contribution of P_o to plant P absorption relative to P_i fractions in P-amended soils remains to be determined. Changes of P_o due to the 14 exhaustive crops grown in the eight soils were observed (Fig. 3). When P was added to raise soil solution P to 0.2 mg L^{-1} , the highly weathered soils (Fig. 3b and 3c) contained more $\text{NaHCO}_3\text{-}P_o$ than the slightly weathered soils (Fig. 3a). This was consistent with the findings of Cross and Schlesinger (1995), who found that within the labile P fraction (strip-P and $\text{NaHCO}_3\text{-}P_i$), the percentage held in organic form ($\text{NaHCO}_3\text{-}P_o$) increased with soil weathering. Significant differences in $\text{NaHCO}_3\text{-}P_o$ were found in soils within each P sorption group for some harvests but not in others, indicating that this fraction fluctuated among harvests (Fig. 3). The NaOH- P_o fraction was greater than the $\text{NaHCO}_3\text{-}P_o$ fraction in all soils (Fig. 3). The NaOH- P_o also seemed to be higher in the highly weathered soils (Fig. 3e and 3f) than in the slightly weathered soils (Fig. 3d), except in the Honouliuli soil, which was the most weathered among the three slightly weathered soils, as indicated by the absence of smectite and the presence of high hematite content (Table 3). The Wahiawa soil generally contained significantly higher NaOH- P_o than the Paaloa soil, but the trend seemed to be reversed after Harvest 10. Among the three high P sorption soils, the Kapaa

soil contained the most NaOH- P_o , while NaOH- P_o in the Leilehua and the Mahana soils was indistinguishable and fluctuated (Fig. 3). Neither $\text{NaHCO}_3\text{-}P_o$ nor NaOH- P_o appeared to change with plant P removal; they fluctuated irregularly. These fluctuations may be due to differences in microbial activities among harvests, or perhaps soil preparation before analysis (Potter et al., 1991). However, when soil available P was greatly depleted by cropping, $\text{NaHCO}_3\text{-}P_o$ appeared to decline with subsequent crop P withdrawal. This was indicated by the decline in $\text{NaHCO}_3\text{-}P_o$ of the Paaloa, Wahiawa, Kapaa, and the Mahana soils after Harvest 10 (Fig. 3). However, no such decline was observed for the NaOH- P_o in those soils. We conclude that P_o was not a significant contributor to soil available P when available P_i was high. When soil P_i was low, such as in the Paaloa and Wahiawa soils after Harvest 10, $\text{NaHCO}_3\text{-}P_o$ began to contribute to available P. Beck and Sanchez (1994) found that P_o did not significantly contribute to plant-available P_i in their Ultisol that received repeated P applications. They suggested that P_i was the major P source for plant growth. In a study involving a toposequence of Lithosols and Cambisols from semiarid northeastern Brazil where native soil P was high, Agbenin and Tiessen (1994) also demonstrated that only 5% of the total P was in organic forms, mostly in stable forms of low availability with little contribution to P fertility. Organic P may be important in P fertility in unfertilized soils or soils with high organic matter, but it does not appear to affect P availability significantly in high-P mineral soils.

Dilute Hydrochloric Acid Extractable Phosphorus

The HCl-P is thought to represent primary mineral P such as apatite (Williams et al., 1980; Tiessen et al., 1984; Tiessen and Moir, 1993) since the Fe- or Al-P that remains unextracted after the NaOH extraction is not soluble in acid (Tiessen and Moir, 1993). The HCl-P is generally assumed to be of low availability to plants, although it was found to decrease in greenhouse studies (Ivarsson, 1990) and in long-term field trials (McKenzie

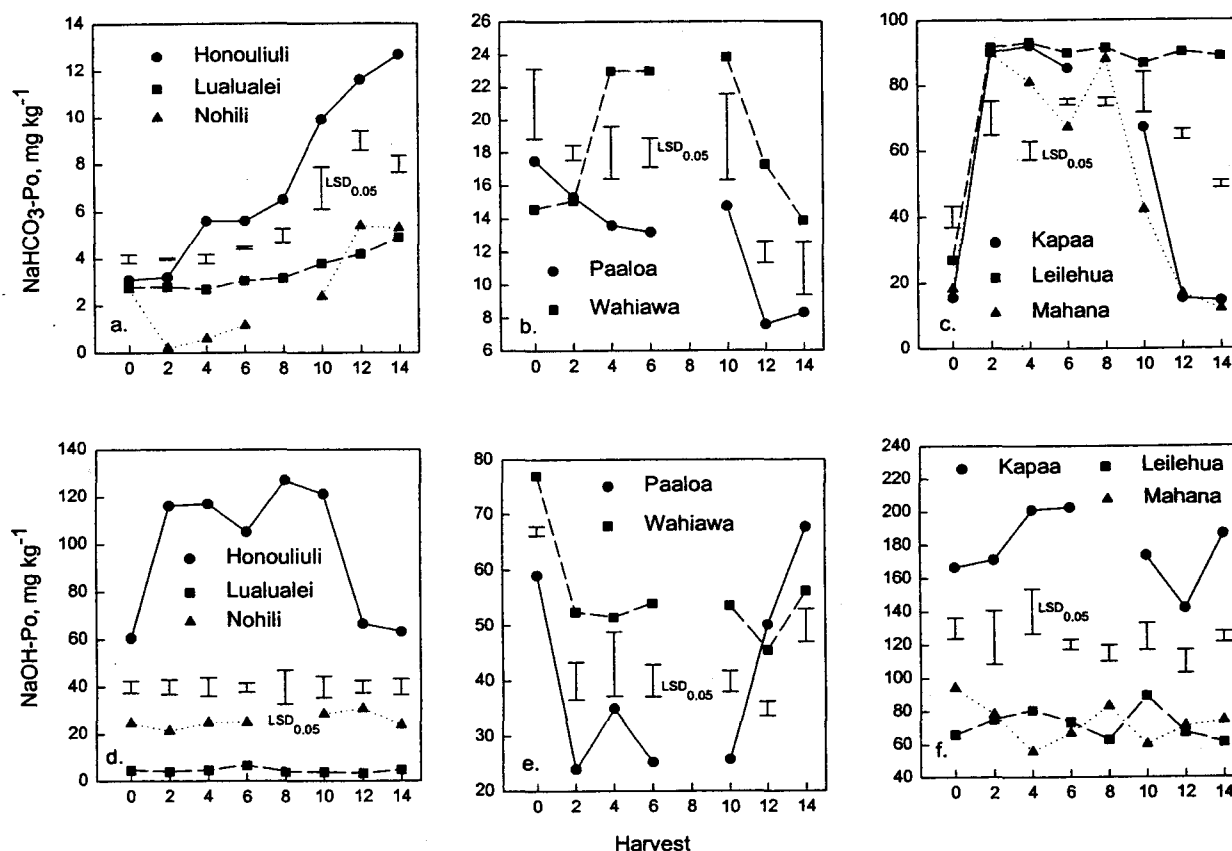


Fig. 3. Changes in organic P in eight soils under exhaustive cropping. Phosphorus was added in each soil to raise soil solution P to 0.2 mg L⁻¹. Honouliuli, Lualualei, and Nohili were considered low P sorption soils and Paaloa and Wahiawa were medium P sorption soils, while the Kapaa, Leilehua, and Mahana soils were characterized by high P sorption.

et al., 1992a). McKenzie et al. (1992b) also reported that HCl-P was increased by fertilizer-P during long-term crop production. However, O'Halloran et al. (1987) observed that P application had no effect on HCl-P in a Brazilian Ultisol (Oxic Haplustult). Laboratory incubation results indicated that HCl-P in the highly weathered soils treated with high P was negligible (Fig. 4c). Changes of HCl-P under exhaustive cropping in soils indicated, as expected, that the slightly weathered soils (Fig. 4a) had high HCl-P, and the highly weathered soils had little (Fig. 4b and 4c), despite the fact that much higher amounts of P were added to the highly weathered soils (1400 mg P kg⁻¹) than to the slightly weathered soils (100 mg P kg⁻¹; Table 4). Among the three slightly weathered soils (Fig. 4a), the Lualualei soil had the most HCl-P, probably because the soil had the highest calcite content (Table 3), followed by the Nohili soil. The Honouliuli soil, which contained no calcite, had the least HCl-P. The HCl-P in the Honouliuli soil may be due to its high exchangeable Ca²⁺ content. The HCl-P declined under exhaustive cropping, especially in the Lualualei soil, which had very high HCl-P (Fig. 4a). This suggested that Ca-P formed with added P was plant available even when available P in soils was high. In the five highly weathered soils, HCl-P was generally <10 mg kg⁻¹ (Fig. 4b and 4c), probably due to the absence of Ca-containing minerals and their low exchangeable Ca²⁺ (data not shown). The detected

HCl-P increase in the highly weathered soils after Harvest 10 (Fig. 4b and 4c) was attributable to Ca-P formed with lime, because prior to planting Crop 11, soils were retested for pH and additional CaCO₃ was added to correct the acidity. Beck and Sanchez (1994) also observed a rapid increase in Ca-P (HCl-P) coinciding with the change in lime source from fast reacting Ca(OH)₂ to slower reacting CaCO₃ in a Paleudult. They found that the Ca-P associated with liming and fertilizer P was among the least stable P compounds in their soil. The subsequent drop in HCl-P after Crop 12 observed in our highly weathered soils (Fig. 4b and 4c) agreed with their findings. In the slightly weathered soils (Fig. 4a), the decline in HCl-P may be caused by the conversion from HCl-P to readily available P (strip-P and NaHCO₃-P_i). The HCl-P may act as a buffer for the available P in the slightly weathered soils similar to the apparent buffering by NaOH-P_i in the highly weathered soils.

Residual Phosphorus Fraction

Changes in residual P under cropping showed two contrasting patterns (Fig. 5). Residual P declined with exhaustive cropping in the three slightly weathered soils (Fig. 5a), but seemed to build up gradually in the highly weathered soils (Fig. 5b and 5c). The slopes of increase were significant at $P < 0.05$. The decline in residual P in slightly weathered soils has been reported in soils

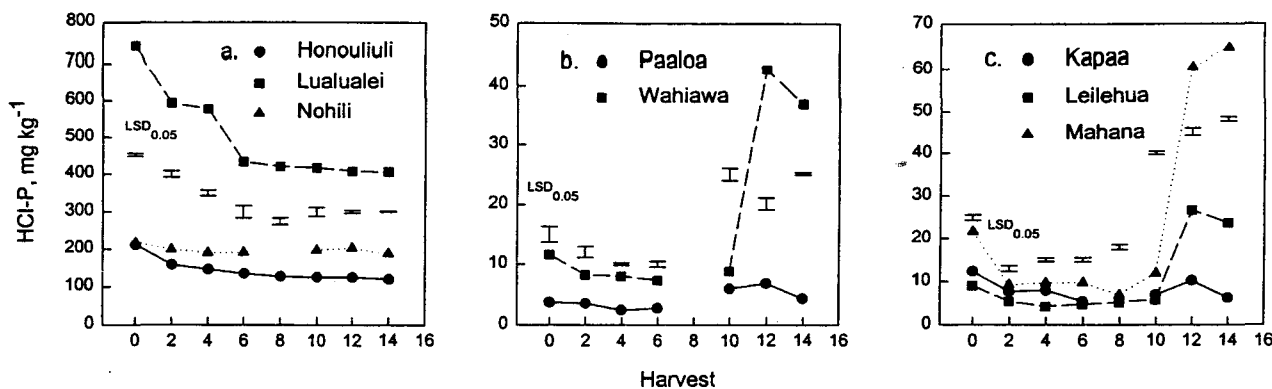


Fig. 4. Changes in HCl-P in eight soils under exhaustive cropping. Phosphorus was added in each soil to raise soil solution P to 0.2 mg L^{-1} . Honouliuli, Lualualei, and Nohili were considered low P sorption soils, Paaloa and Wahiawa were medium P sorption soils, while the Kapaa, Leilehua, and Mahana soils were characterized by high P sorption.

similar to ours (Hedley et al., 1982; McKenzie et al., 1992a, 1992b). Higher residual P was observed in the slightly weathered soils than in the highly weathered soils when the same amount of P was added. We postulated that some residual P in the slightly weathered soils was Ca-P, which was not removed because all extractants prior to the 1 M HCl solution were alkaline. However, this Ca-P may act as a buffer for readily available P. When the readily available P is withdrawn, Ca-P in the residual fraction may be mobilized to replenish the available P. This may explain the gradual decline in residual P in the three slightly weathered soils (Fig. 5a). This explanation was further strengthened by the relatively faster decline of the residual P in the Lualualei soil (Fig. 5a), which has a higher calcite content and thus probably more Ca-P.

However, in the highly weathered soils, the residual P fraction not only failed to decrease during plant P withdrawal, but it continued to increase with time (Fig. 5b and 5c). Similar results have not been reported. Previous experiments either lacked the time required to observe the change or were complicated by repeated P applications. However, a lack of accumulation in the residual P fraction has been reported by Beck and Sanchez (1994) on a Paleudult. Their Ultisol, nonetheless, was not a typical highly weathered soil. It had low P sorption capacity and needed only 24 mg P kg^{-1} to raise

solution P to 0.2 mg L^{-1} . In addition, the clay fraction of that soil contained 90% layer silicates and 10% Fe and Al oxides (Beck and Sanchez, 1994). The "slow reaction" (Barrow, 1980) in Beck and Sanchez's soil may be negligible, and conversion of available P to residual P may not be a major process. In contrast, the mineralogy of our highly weathered soils was dominated by high P-affinitive Fe and Al oxides and amorphous materials (Table 3). Therefore, the continued buildup in residual P in the highly weathered soils was not surprising.

CONCLUSIONS

The results indicated that strip-P and $\text{NaHCO}_3\text{-P}_i$ were most sensitive to plant P withdrawal in all soils. The NaOH-P_i also declined with plant P removal in all soils. The HCl-P and residual P in the slightly weathered soils declined under cropping and were major P fractions in the slightly weathered soils possibly acting as a buffer for the strip-P and $\text{NaHCO}_3\text{-P}_i$ in these soils. The NaOH-P_i was the dominant P fraction in the highly weathered soils, and declined in response to plant P removal. The NaOH-P_i and strip-P and $\text{NaHCO}_3\text{-P}_i$ appeared to be in equilibrium. When strip-P and $\text{NaHCO}_3\text{-P}_i$ were high, NaOH-P_i accumulated or remained stable despite plant P removal; when strip-P and $\text{NaHCO}_3\text{-P}_i$ were reduced by plant removal, NaOH-P_i

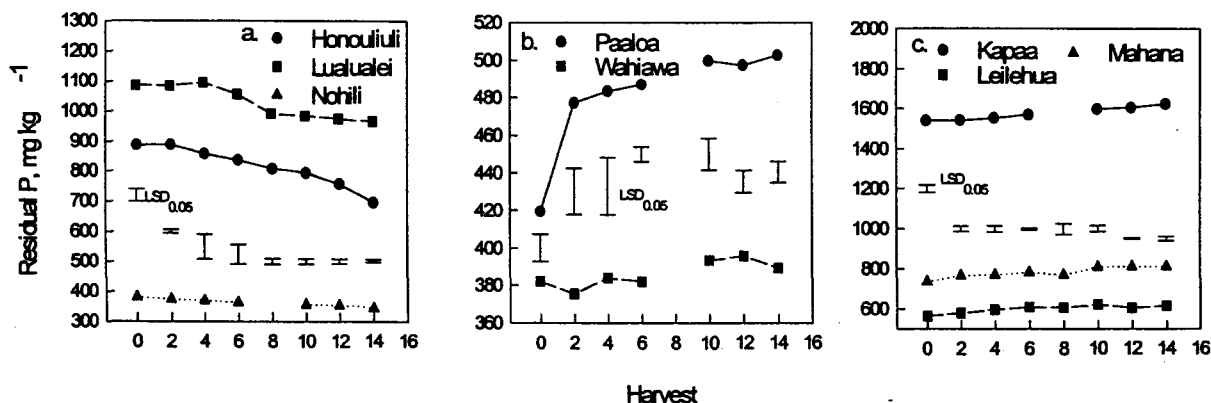


Fig. 5. Changes in residual P in eight soils under exhaustive cropping. Phosphorus was added in each soil to raise soil solution P to 0.2 mg L^{-1} . Honouliuli, Lualualei, and Nohili were considered low P sorption soils and Paaloa and Wahiawa were medium P sorption soils, while the Kapaa, Leilehua, and Mahana soils were characterized by high P sorption.

P_i decreased, and then further declines in strip-P and $NaHCO_3$ - P_i occurred. The $NaOH$ - P_i appeared to act as a buffer for strip-P and $NaHCO_3$ - P_i in the highly weathered soils. In the slightly weathered soils, residual P declined in response to plant P removal, suggesting that in such soils residual P may contain plant-available P. In contrast, residual P in the highly weathered soils accumulated with plant P removal, suggesting that it was unavailable to plants. Organic P was not critical to P availability in our soils that received high P inputs. The same P fraction, therefore, differed in availability in different soils.

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REFERENCES

- Agbenin, J.O., and H. Tiessen. 1994. Phosphorus transformations in a toposequence of Lithosols and Cambisols from semi-arid northern Brazil. *Geoderma* 62:345-362.
- American Public Health Association (APHA), American Water Works Association (AWWA), and Water Environment Federation (WEF). 1995. 4500-P Phosphorus. p. 4-110. In A.D. Eaton et al. (ed.) Standard methods for the examination of water and wastewater. 19th ed. APHA Publ. Office, Washington, DC.
- Barrow, N.J. 1980. Evaluation and utilization of residual phosphorus in soil. p. 333-359. In F.E. Khasawneh et al. (ed.) The role of phosphorus in agriculture. ASA, CSSA, and SSSA, Madison, WI.
- Ball-Coelho, B., I.H. Salcedo, H. Tiessen, and J.W.B. Stewart. 1993. Short- and long-term phosphorus dynamics in a fertilized Ultisol under sugarcane. *Soil Sci. Soc. Am. J.* 57:1027-1034.
- Beck, M.A., and P.A. Sanchez. 1994. Soil phosphorus fraction dynamics during 18 years of cultivation on a Typic Paleudult. *Soil Sci. Soc. Am. J.* 58:1424-1431.
- Bowman, R.A., S.R. Olsen, and F.S. Watanabe. 1978. Greenhouse evaluation of residual phosphate by four phosphorus methods in neutral and calcareous soils. *Soil Sci. Soc. Am. J.* 42:451-454.
- Cross, A.F., and W.H. Schlesinger. 1995. A literature review and evaluation of the Hedley fractionation: Applications to the biogeochemical cycles of soil phosphorus in natural ecosystems. *Geoderma* 64:197-214.
- Fox, R.L., and E.J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the phosphate requirements of soils. *Soil Sci. Soc. Am. Proc.* 34:902-907.
- Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383-411. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Guo, F., R.S. Yost, and R.C. Jones. 1996. Evaluating iron-impregnated paper strips for assessing available soil phosphorus. *Commun. Soil Sci. Plant Anal.* 27:2561-2590.
- Hedley, M.J., W.B. Stewart, and B.S. Chauhan. 1982. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 46:970-976.
- Hodges, S.C., and L.W. Zelazny. 1980. Determination of noncrystalline soil components by weight difference after selective dissolution. *Clays Clay Miner.* 28:35-42.
- Hsu, P.H. 1965. Fixation of phosphate by aluminum and iron in acidic soils. *Soil Sci.* 99:398-402.
- Ivarsson, K. 1990. The long-term soil fertility experiments in southern Sweden. IV. Changes in inorganic and organic soil after a pot trial. *Acta Agric. Scand.* 40:205-215.
- Iyamuremye, F., R.P. Dick, and J. Baham. 1996. Organic amendment and phosphorus dynamics: II. Distribution of soil phosphorus fractions. *Soil Sci.* 161:436-443.
- Jones, R.C., C.J. Babcock, and W.B. Knowlton. 2000. Estimation of the total amorphous content in Hawaii soils by the Rietveld method. *Soil Sci. Soc. Am. J.* 64:1100-1108.
- Leinweber, P. 1996. Phosphorus fractions in soils from an area with high density of livestock population. *Z. Pflanzenernaehr. Bodenkd.* 159:251-256.
- Mattingly, G.E.G. 1975. Labile phosphate in soils. *Soil Sci.* 119:369-375.
- McKenzie, R.H., J.W.B. Stewart, J.F. Dormaar, and G.B. Schaallje. 1992a. Long-term crop rotation and fertilizer effects on phosphorus transformations. II. In a Luvisolic soil. *Can. J. Soil Sci.* 72:581-589.
- McKenzie, R.H., J.W.B. Stewart, J.F. Dormaar, and G.B. Schaallje. 1992b. Long-term crop rotation and fertilizer effects on phosphorus transformations. I. In a Chernozemic soil. *Can. J. Soil Sci.* 72:569-579.
- McLaughlin, J.R., J.C. Ryden, and J.K. Syers. 1977. Development and evaluation of a kinetic model to describe phosphorus sorption by hydrous ferric oxide gels. *Geoderma* 18:295-307.
- Menon, R.G., L.L. Hammond, and H.A. Sissingh. 1989. Determination of plant available phosphorus by the iron hydroxide-impregnated filter paper (Pi) soil test. *Soil Sci. Soc. Am. J.* 53:110-115.
- Murphy, J.P., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta* 27:31-36.
- Nelson, R.E. 1982. Carbonates and gypsum. p. 181-197. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Nelson, R.E., and L.E. Sommers. 1982. Total carbon, organic carbon, and organic matter. p. 539-579. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Olsen, S.R., and L.E. Sommers. 1982. Phosphorus. p. 403-430. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- O'Halloran, I.P., J.W.B. Stewart, and R.G. Kachanoski. 1987. Influence of texture and management practices on the forms and distribution of soil phosphorus. *Can. J. Soil Sci.* 67:147-163.
- Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990a. Phosphorus chemistry and mineralogy in excessively fertilized soils: Quantitative analysis of phosphorus-rich particles. *Soil Sci. Soc. Am. J.* 54:1576-1583.
- Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990b. Phosphorus chemistry and mineralogy in excessively fertilized soils: Descriptions of phosphorus-rich particles. *Soil Sci. Soc. Am. J.* 54:1583-1589.
- Pierzynski, G.M., T.J. Logan, S.J. Traina, and J.M. Bigham. 1990c. Phosphorus chemistry and mineralogy in excessively fertilized soils: Solubility equilibria. *Soil Sci. Soc. Am. J.* 54:1589-1595.
- Potter, R.L., C.F. Jordan, R.M. Guedes, G.J. Batmanian, and X.G. Han. 1991. Assessment of a phosphorus fraction method for soil: Problems for further investigation. *Agric. Ecosyst. Environ.* 34:453-463.
- Richards, J.E., T.E. Bates, and S.C. Sheppard. 1995. Changes in the forms and distribution of soil phosphorus due to long-term corn production. *Can. J. Soil Sci.* 75:311-318.
- Ryden, J.C., J.R. McLaughlin, and J.K. Syers. 1977. Mechanisms of phosphate sorption of soils and hydrous ferric oxide gel. *J. Soil Sci.* 28:72-92.
- SAS Institute. 1996. SAS/STAT users' guide. Version 6. SAS Inst., Cary, NC.
- Sawhney, B.L. 1973. Electron microprobe analysis of phosphate in soils and sediments. *Soil Sci. Soc. Am. Proc.* 37:658-660.
- Schmidt, J.P., S.W. Buol, and E.J. Kamprath. 1996. Soil phosphorus dynamics during seventeen years of continuous cultivation: Fractionation analysis. *Soil Sci. Soc. Am. J.* 60:1168-1172.
- Sharpley, A.N. 1991. Soil phosphorus extracted by iron-aluminum-oxide-impregnated filter paper. *Soil Sci. Soc. Am. J.* 55:1038-1041.
- Sharpley, A.N., H. Tiessen, and C.V. Cole. 1987. Soil phosphorus forms extracted by soil tests as a function of pedogenesis. *Soil Sci. Soc. Am. J.* 51:362-365.
- Sietronics Pty., Ltd. 1993. The new SIROQUANT for Windows manual. v. 1.20. Canberra, Australia.
- Thomas, G. 1982. Exchangeable cations. p. 159-165. In A.L. Page et al. (ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Tiessen, H., and J.O. Moir. 1993. Characterization of available P by sequential extraction. p. 75-86. In M.R. Carter (ed.) Soil sampling and methods of analysis. Canadian Society of Soil Science. Lewis Publ., Boca Raton, FL.

- Tiessen, H., J.W.B. Stewart, and C.V. Cole. 1984. Pathways of phosphorus transformation in soils of differing pedogenesis. *Soil Sci. Soc. Am. J.* 48:853-858.
- Tiessen, H., J.W.B. Stewart, and J.O. Moir. 1983. Changes in organic and inorganic phosphorus composition of two grassland soils and their particle size fractions during 60-90 years of cultivation. *J. Soil Sci.* 34:815-823.
- van der Zee, S.E.A.T.M., L.G.J. Fokkink, and W.H. van Riemsdijk. 1987. A new technique for assessment of reversibly adsorbed phosphate. *Soil Sci. Soc. Am. J.* 51:599-604.
- Wager, B.I., J.W.B. Stewart, and J.O. Moir. 1986. Changes with time in the form and availability of residual fertilizer phosphorus on Chernozemic soils. *Can. J. Soil Sci.* 66:105-119.
- Webber, M.D. 1978. Effects of temperature and time on hydroxy aluminum phosphate-montmorillonite complex. *Soil Sci.* 125: 107-114.
- Williams, J.D.H., T. Mayer, and J.O. Nriagu. 1980. Extractability of phosphorus from phosphate minerals common in soils and sediments. *Soil Sci. Soc. Am. J.* 44:462-465.
- Williams, J.D.H., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1971. Fractionation of inorganic phosphate in calcareous lake sediments. *Soil Sci. Soc. Am. Proc.* 35:250-255.
- Yost, R.S., A.B. Onken, F. Cox, and S. Reid. 1992. The diagnosis of phosphorus deficiency and predicting phosphorus requirement. Univ. of Hawaii, Honolulu.